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(54) Etching resist composition, pattern forming method making use of the same, printed-wiring board and its production.

(57) An etching resist composition containing at least a polymeric compound having an acid value of not less than 35, a base, and water, and having a viscosity of 10 centipoises or below.

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BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a novel composition having etching resist properties, a pattern forming method making use of the composition, a printed-wiring board and a process for producing the printed-wiring board.

More particularly, this invention is concerned with printed-wiring board processing in which, in forming a copper printed-wiring pattern, a resist pattern for etching a copper-clad laminate is directly drawn on copper foil by ink-jet printing.

Related Background Art

In conventional subtractive processes used in printed-wiring board processing, wiring patterns are formed by preparing pattern films by means of a laser plotter in accordance with wiring pattern data outputted from a CAD (computer-aided design system), and etching copper foil by using a resist ink or a dry film resist.

In such conventional processes, it is necessary to first form a pattern film, and to prepare a printing plate in the case when a resist ink is used or to take the steps of lamination, exposure and development in the case when a dry film resist is used.

Such methods currently used can be said to be a method in which the digitised wiring data are returned to an analogic image forming step. Screen printing has a limit to work size because of the printing precision of the plate. The dry film process is a photographic process and, though promising a high precision, requires many steps, inevitably resulting in a reasonably high cost especially for the manufacture in small lot.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a pattern forming method, a process for producing a printed-wiring board and an etching resist composition used therein, that can decrease the number of steps for forming copper printed wiring patterns and can achieve a cost reduction.

Another object of the present invention is to provide an etching resist composition that enables printing on a substrate having no liquid-absorption, enables stripping of resist patterns printed, and has etching resist properties.

The above objects of the present invention can be achieved by the invention described below.

The present invention is an etching resist composition comprising a polymeric compound having an acid value of not less than 35, a base, and water, and having a viscosity of 10 centipoises or below.

In another embodiment, the present invention is an etching resist composition comprising a polymeric compound having an acid value of not less than 35, a number average molecular weight of not more than 40,000 and a glass transition temperature of 60 °C or above, a base, and water, and having a viscosity of 10 centipoises or below.

In a preferred embodiment of the present invention, the etching resist composition further contains a silicone type surface active agent or contains a thixotropic compound, contains a base having a boiling point of 190 °C or below at normal pressure and further contains a coloring material.

The present invention is also a pattern forming method comprising the steps of;

patternwise imparting the etching resist composition described above to the surface of a substrate by ink-jet printing; and

evaporating the solvent of the composition patternwise imparted.

The present invention is still also a process for producing a printed-wiring board, comprising the steps of;

patternwise imparting the etching resist composition described above to the surface of a copper-foil laminated substrate by ink-jet printing;

evaporating the solvent of the composition patternwise imparted; and

etching the copper foil.

The process may further comprise the step of removing the etching resist composition pattenwise formed.

The present invention is further a printed-wiring board obtained by the production process described above.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides a technique for printing an etching resist pattern on a copper-clad laminate by a digital image recording system directly from wiring data prepared by CAD.

In the present invention, the use of the etching resist composition described above makes it possible to obtain superior pattern forming performance, etching resist properties and post-etching strippability. A volatile base may also be used to dissolve the polymeric compound, whereby better etching resist properties can be obtained. In the etching resist composition, a silicone type surface active agent and/or a thixotropic compound may be incorporated. The incorporation of these makes it possible to obtain a clearer pattern form as copper printed-wiring on the copper-clad laminate. More specifically, when this composition is ejected onto a usual brush-polished copper-clad laminate to print a resist pattern, the composition has a wetting-spreadability such that a pattern can be drawn in a given form and size without being affected by polish marks on the surface. The resist pattern formed at the same time serves as a copper foil etching resist and has a resistance to both acidic etchants and alkaline etchants, in other words, a resistance to chemical matter and an adhesion to substrates. Incorporation of a monohydric alcohol into this composition improves bubble generation and drop ejection performance in bubble jet type ink-jet printing and brings about a stabler printing suitability.

The polymeric compound used in the etching resist composition of the present invention includes the following.

(1) Alkali-soluble acrylic resins obtained by copolymerization of a carboxyl group-containing monomer such as acrylic acid, methacrylic acid, crotonic acid or maleic acid with styrene or an alkyl acrylate.

(2) Alkali-soluble polymers of polyether, polyester or polyurethane having a carboxyl group side chain in the molecular chain.

(3) Maleic acid addition compounds of rosin or rosin derivatives.

(4) Polysaccharides containing a carboxyl group.

These compounds are neutralized by a base to form compounds readily soluble in water. The base used can be exemplified by ammonia, methylamine, ethylamine, dimethylamine, diethylamine, n-butylamine, di-n-butylamine, trimethylamine, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, propylenediamine, ethanolamine, hexylamine, laurylamine, diethanolamine, triethanolamine, morpholine, piperidine, propylamine, isopropylamine, isobutylamine, NaOH, LiOH and KOH. Here, as the base used, organic bases are preferred in order to endow the etching resist composition with the chemical resistance to etchants or etching solutions and to make the etching resist composition strippable from the substrate by a strong alkali. Among these, bases having a high volatility are particularly preferred, and bases having themselves a boiling point of 190 °C or below at normal pressure are preferred.

The resin applied to the surface of a copper-clad laminate by printing becomes insoluble to acidic etchants as a result of evaporation of volatile bases such as ammonia and also becomes not easily soluble to basic etchants to have resistance to etching solutions, so that it has etching resist properties. The polymeric compound contained in the composition has an acid value and can be still dissolved in, or stripped by, strongly alkaline stripping solutions used after etching. A solubility difference with respect to this basicity is utilized so that the composition can have both etching resist properties and stripping performance.

- Polymeric Compound with Acid Value -

The alkali-soluble acrylic resin used as the polymeric compound having an acid value of not less than 35 includes alkali-soluble acrylic resins obtained by copolymerization of a carboxyl group-containing monomer such as acrylic acid, methacrylic acid, crotonic acid or maleic acid with styrene, an alkyl acrylate or an acrylic or methacrylic ester having a hydroxyl group as exemplified by 2-hydroxyethyl acrylate or methacrylate. Theoretically, the polymeric compound having an acid value of 35 can be produced using, in the case of acrylic acid, 4.5% by weight of acrylic acid as percentage of monomers charged in polymerization. If the acid value is too low, the resin can not be dissolved only by its neutralization with the base, and requires use of other polar solvent in combination. These acrylic resins may preferably have a glass transition temperature (Tg) of 60 °C or above in view of its relation to ethcing temperature, and preferably be a polymer having a number average molecular weight of not more than 40,000 in order to control the viscosity of the composition and make the composition dissolve with ease.

Examples of specific structures of these are the following copolymers.

A-1: Acrylic acid/methyl methacrylate = 10/90 Theoretical acid value: 78; weight average molecular weight: 15,000; Tg: 98 °C.

A-2: Acrylic acid/ethyl methacrylate/2-hydroxyethyl acrylate = 15/60/25 Theoretical acid value: 117; weight average molecular weight: 20,000; Tg: 77 °C.

A-3: Acrylic acid/styrene/2-hydroxyethyl acrylate = 5/70/25 Theoretical acid value: 39; weight average molecular weight: 16,500; Tg: 83 °C.

A-4: Methacrylic acid/methyl methacrylate/2-hydroxyethyl acrylate = 25/60/15 Theoretical acid value: 163; weight average molecular weight: 35,000; Tg: 105 °C.

Saturated polyesters having an acid value are also materials preferable as the polymeric compound used in the present invention. Starting materials for the saturated polyesters may be the same as materials hitherto used in coating compositions and inks. To impart the acid value thereto, polybasic acids such as trimellitic anhydride may be used so that free acids remain, whereby they can be readily synthesized.

The starting materials for the saturated polyesters include polyhydric alcohols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol and oligomers of these, trimethylol propane, pentaerythritol, dimethylol propionic acid, trishydroxyaminomethane, trishydroxyaminoethane, and aliphatic dibasic acids such as succinic acid, adipic acid, orthophthalic anhydride and trimellitic anhydride.

Examples of these compounds are as follows:

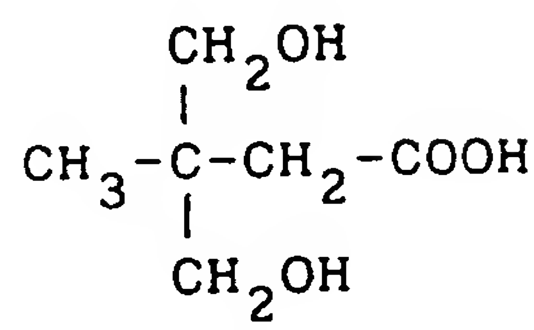
B-1: Oligoesters with a molecular weight of 500, comprised of ethylene glycol, orthophthalic anhydride and succinic anhydride and having a hydroxyl group at the terminal, having been subjected to chain extension by the use of trimellitic anhydride to impart carboxyl groups at the same time. Theoretically, six carboxyl groups per molecule are introduced to obtain polyesters with an average molecular weight of 2,700, having a hydroxyl group at the terminal.

B-2: Oligoesters with a molecular weight of 600, comprised of 1,4-butanediol and adipic acid, having been subjected to chain extension by the use of trimellitic anhydride to impart carboxyl groups at the same time. Theoretically, six carboxyl groups per molecule are introduced to obtain polyesters with an average molecular weight of 2,700, having a hydroxyl group at the terminal.

Polyurethanes having an acid value are also preferable materials used as the polymeric compound used in the present invention. The polyurethanes may be formed of either polyether or polyester as the basic structure, and those hitherto commonly used can be used. To impart the acid value thereto, compounds having two hydroxyl groups and one carboxyl group in the molecule, as shown in Exemplary Compounds 1 to 6 below, may be used so as to make free acids remain in the molecular chain.

Materials for imparting acid value:

Exemplary Compound 1



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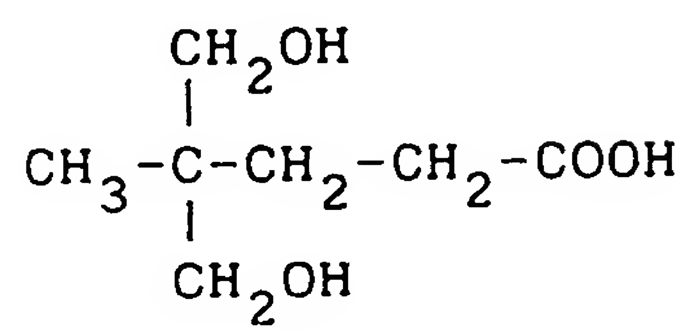
Exemplary Compound 2



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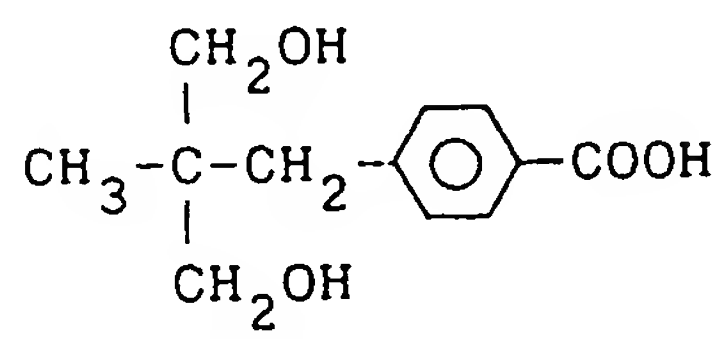
Exemplary Compound 3



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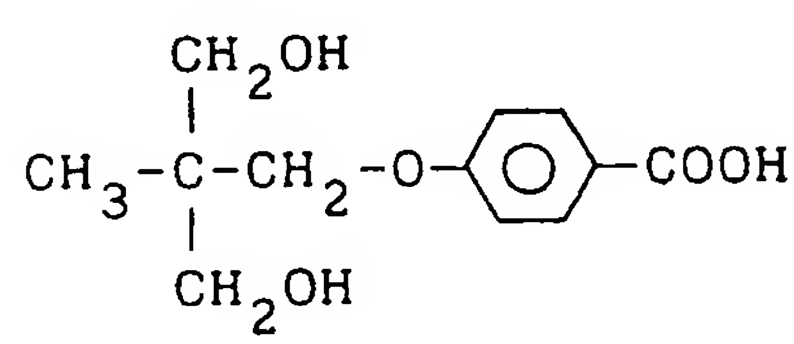
Exemplary Compound 4



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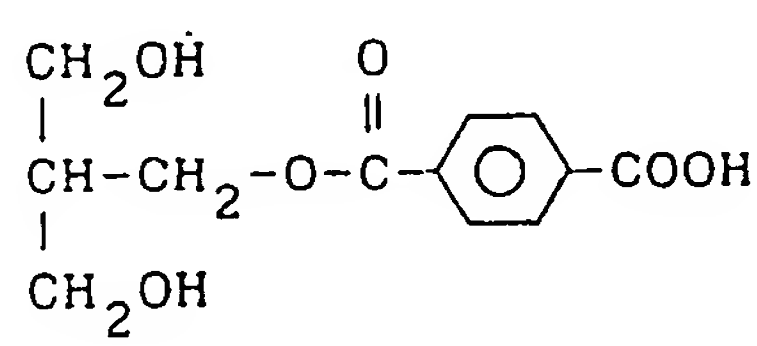
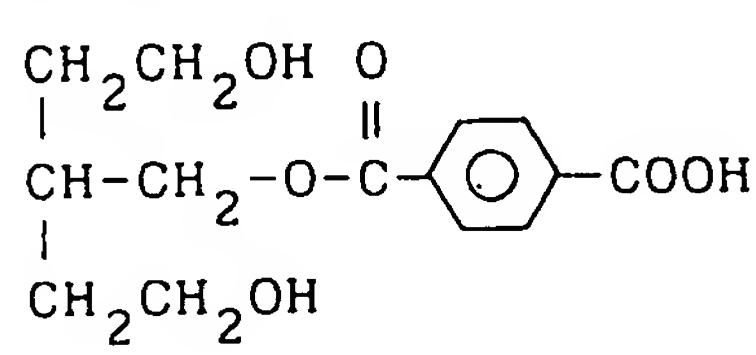
Exemplary Compound 5



, and

Exemplary Compound 6



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Specific compounds obtained in this way and used in the present invention are materials as shown below.

C-1: Polyethylene glycol (molecular weight: 400), dimethylolpropionic acid and 1,4-tolylene diisocyanate are reacted with each other in equimolar quantities to obtain a polyurethane with an average molecular weight of 3,000, having an acid value.

C-2: Polypropylene glycol (molecular weight: 400), Exemplary Compound 5 and 1,4-tolylene diisocyanate are reacted with each other in equimolar quantities to obtain a polyurethane with an average molecular weight of 3,000, having an acid value.

Natural materials having an acid value are also useful in the present invention. As examples thereof, they include rosin (acid value: 90 to 180), polymer rosin (acid value: 150 or less), hydrogenated rosin (acid value: 160 or less), disproportionated rosin (acid value: 150 or less) , adducts of rosin with an α,β-unsaturated dicarboxylic acid, alkyd resins, and adducts of terpene with an α,β-unsaturated dicarboxylic acid. Here, the α,β-unsaturated dicarboxylic acid may include maleic acid, fumaric acid, citraconic acid, itaconic acid, mesaconic acid and aconitic acid.

Incorporation of a silicone type surface active agent into the composition having etching resist properties enables control of wetting-spreadability when the resist pattern is printed on the copper-clad laminate, so that preferable dot forms can be obtained. The silicone type surface active ,agent used here may include nonionic surface active agents having an ethylene oxide chain as a hydrophilic group and a dimethyl siloxane chain as a silicone chain. These materials can be selected from those commercially available when used.

Incorporation of a thixotropic compound into the composition of the present invention also enables control of wetting-spreadability, so that preferable dot forms can be obtained. This thixotropic compound is a generic term of compounds having the action to thicken, agglomerate or gelatinize compositions containing water, as typified by dibenzylidene sorbitol, alginic acid and chitosan. When the composition containing such a compound is used, droplets ejected and impacted onto the substrate can quickly thicken as a result of slight evaporation of water or as a result of evaporation of mediums accelerated by previously heating the substrate, so that unwanted spread of dots can be prevented to make it easy to control pattern form and size

- Coloring Material -

In the liquid mixture having etching resist properties of the present invention, a coloring material may be dissolved or dispersed in order to make printed patterns visible. It may be selected from high-purity dyes having been hitherto developed as dyes for ink-jet recording, including acid dyes, direct dyes, basic dyes, oil-soluble dyes, disperse dyes, reactive dyes and food dyes. Examples thereof are, when printed patterns are colored in blue as commonly done in resist inks, C.I. Direct Blue 86, C.I. Direct Blue 199, C.I. Acid Blue 9 and C.I. Oil Blue 9.

- Medium -

The etching resist composition of the present invention makes use of water as a main medium.

As mediums other than water, any of water-soluble organic solvents having a high wettability, capable of being evaporated with difficulty and having a good hydrophilicity can be added. It is possible to use ethylene glycol, diethylene glycol, triethylene glycol, tripropylene glycol, glycerol, 1,2,4-butanetriol, 1,2,6-hexanetriol, 1,2,5-pentanetriol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, dimethylsulfoxide, diacetone alcohol, glycerol monoallyl ether, propylene glycol, butylene glycol, polyethylene glycol 300, thiodiglycol, N-methyl-2-pyrrolidone, 2-pyrrolidone, γ-bytyrolactone, 1,3-dimethyl-2-imidazolidinone,sulforane, trimethylol propane, neopentyl glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monoisopropyl ether, ethylene glycol monoallyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monoethyl ether, β-dihydroxyethylurea, urea, acetonyl acetone, pentaerythritol, 1,4-cyclohexanediol, hexylene glycol, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethylene glycol monoisobutyl ether, ethylene glycol monophenyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, diethylene glycol monoisobutyl ether, triethylene glycol monobutyl ether, triethylene glycol dimethyl ether, triethylene glycol diethyl ether, tetraethylene glycol dimethyl ether, tetraethylene glycol diethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, glycerol monoacetate, glycerol diacetate, glycerol triacetate, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether acetate, cyclohexanol, 1,2-cyclohexanediol, 1-butanol, 3-methyl-1,5-pentanediol, 3-hexene-2,5-diol, 2,3-butanediol, 1,5-pentanediol, 2,4-pentanediol, 2,5-hexanediol, ethanol, n-propanol, 2-propanol, 1-methoxy-2-propanol, furfuryl alcohol, and tetrahydrofurfuryl alcohol. The water soluble organic solvents may preferably be used in a total amount of from 5 to 40% by weight based on the weight of the whole composition. Since, however, these solvents can be removed with difficulty and may affect resist properties, they may preferably be used in an amount as small as possible.

The respective components in the composition having etching resist properties of the present invention may be mixed in such a proportion that the polymeric compound having an acid value is added in an

amount of from 3 to 20% by weight in the composition and the corresponding base is in an amount not smaller than the equivalent weight calculated from the acid value. As a whole, the viscosity of the composition is controlled so as not to be more than 10 centipoises.

In the composition of the present invention, it is unnecessary to use any particular adhesion improver. It, however, is possible to use the above resin in combination, which is effective for delicate adjustment of softening temperatures and strippability. Acrylic resins and rosin derivatives are effective for improving hardness of resist coatings, and polyester resins and urethane resins for improving adhesion thereof. The silicone type surface active agent can be effective when used so far as it can dissolve, i.e., in an amount of not more than about 0.5% by weight; and the thixotropic compound, so far as the viscosity is ensured, i.e., in an amount of not more than about 1.0% by weight.

The pattern forming method and the process for producing a printed-wiring board according to the present invention are carried out in the following way.

A copper-clad laminate for the printed-wiring board is surface-conditioned as usual (e.g., by chemical polishing, brush polishing or sandblasting), followed by drying. The etching resist composition of the present invention is charged in an ink-jet recording device to make a print in a wiring pattern on the substrate. The substrate on which the pattern has been printed is dried to remove the medium. The substrate on which a resist pattern has been thus formed is etched using a copper etching solution of a ferric chloride type, cupric chloride type or ammonium persulfate type. From the substrate having been thus etched, the resist is stripped by means of a resist stripping device making use of sodium hydroxide or an organic alkali.

The present invention will be described below in greater detail by giving Examples. In the following, "part(s)" refers to "part(s) by weight".

Example 1

An etching resist composition was prepared using the following components.

Rosin-modified maleic acid resin (acid value: 135)	10 parts
Ammonia	0.7 part
Water	90 parts
C.I. Direct Blue 86	0.2 part.

This composition had a viscosity of 7.5 cP. This composition was charged in an ink-jet printer of a system in which the number of nozzles is 48, resolution in the directions of primary and secondary scanning is 600 dpi, droplet volume is 35 pl and a piezoelectric element with a drive frequency of 4 kHz is used as an ejection energy generating element. Using this printer, an etching resist pattern was printed on a copper-clad laminate for a printed-wiring board having been brush-polished (for public use; one-side copper foil thickness: 35 µm; substrate thickness: 1.2 mm). The wiring pattern was dot-printed in accordance with printing data prepared from wiring pattern data previously made up. The wiring pattern thus printed had a wiring width of about 155 rim and a pad diameter of 1.0 mm. After the pattern formed of the composition in a wiring form was printed, the substrate was heat-dried in a 85 °C oven for 15 minute to remove solvent components. After the substrate was cooled, etching was carried out using a ferric chloride type etching solution and a copper chloride type etching solution each. The etching was carried out at 50 °C for 4 minutes by spraying. After the etching, the resulting substrate was washed with water and wiring width was measured to obtain the results that the width of copper wiring was, on the average, as follows:

In the case of the ferric chloride type etching solution; wiring with: 123 µm, pad diameter: 0.94 mm; and in the case of the copper chloride type etching solution, wiring with: 120 µm, pad diameter: 0.92 mm.

Example 2

An etching resist composition was prepared using the following components.

Acrylic resin (A-1) (Acid value: 140)	10 parts
Ammonia	0.7 part
Water	90 parts
C.I. Direct Blue 86	0.2 part.

This composition had a viscosity of 4.5 cP.

Example 3

An etching resist composition was prepared using the following components.

Polyester resin (B-1) (Acid value: 125)	10 parts
Ammonia	0.7 part
Water	90 parts
C.I. Direct Blue 86	0.2 part.

This composition had a viscosity of 4.3 cP.

The foregoing compositions of Examples 2 and 3 were tested in the same manner as in Example 1. As a result, like Example 1, good etching resist properties and strippability were shown.

Example 4

An etching resist composition was prepared using the following components.

Polyurethane resin (C-1) (Acid value: 95)	10 parts
Ammonia	0.5 part
Diethylene glycol	30 parts
Isopropyl alcohol	5 parts
Water	50 parts
C.I. Direct Blue 86	0.2 part.

This composition had a viscosity of 6.5 cP.

Example 5

An etching resist composition was prepared using the following components.

Polyurethane resin (C-1) (Acid value: 60)	10 parts
Ammonia	0.5 part
N-methylpyrrolidone	30 parts
Isopropyl alcohol	5 parts
Water	50 parts
C.I. Direct Blue 86	0.2 part.

This composition had a viscosity of 5.5 cP.

The compositions of Examples 4 and 5 were each charged in an ink-jet printer of a bubble jet system in which the number of nozzles is 128, resolution in the directions of primary and secondary scanning is 600 dpi, droplet volume is 35 pl and drive frequency is 4 kHz. Subsequently, resist patterns were formed in the same manner as in Example 1 and etching and stripping were tested similarly. As a result, like Example 1, good resist properties and strippability were shown.

As described above, the present invention can provide an etching resist composition having superior etching resist properties and post-etching strippability.

Imparting such an etching resist composition to the surface of a substrate by ink-jet printing can provide a printed-wiring board through steps less in number than those in conventional methods and also with a cost reduction.

An etching resist composition containing at least a polymeric compound having an acid value of not less than 35, a base, and water, and having a viscosity of 10 centipoises or below.

Claims

1. An etching resist composition comprising a polymeric compound having an acid value of not less than 35, a base, and water, and having a viscosity of 10 centipoises or below.

2. An etching resist composition comprising a polymeric compound having an acid value of not less than 35, a number average molecular weight of not more than 40,000 and a glass transition temperature of 60 °C or above, a base, and water, and having a viscosity of 10 centipoises or below.

3. The etching resist composition according to claim 1 or 2, wherein said polymeric compound is contained in an amount ranging from 3% by weight to 20% by weight.

4. The etching resist composition according to claim 1 or 2, which further comprises a silicone type surface active agent.

5. The etching resist composition according to any one of claims 1 to 4, which further comprises a thixotropic compound.

6. The etching resist composition according to any one of claims 1 to 5, wherein said base has a boiling point of 190 °C or below at normal pressure.

7. The etching resist composition according to any one of claims 1 to 6, which further comprises a coloring material.

8. A pattern forming method comprising the steps of;
   patternwise imparting the etching resist composition according to any one of claims 1 to 7 to the surface of a substrate by ink-jet printing; and
   evaporating the solvent of the composition patternwise imparted.

9. The pattern forming method according to claim 8, wherein said ink-jet printing is of a bubble jet system.

10. A process for producing a printed-wiring board, comprising the steps of;
    patternwise imparting the etching resist composition according to any one of claims 1 to 7 to the surface of a copper-foil laminated substrate by ink-jet printing;
    evaporating the solvent of the composition patternwise imparted; and
    etching the copper foil.

11. The process for producing a printed-wiring board according to claim 10, wherein said ink-jet printing is of a bubble jet system.

12. The process for producing a printed-wiring board according to claim 10, which further comprises the step of removing the etching resist composition pattenwise formed.

13. A printed-wiring board obtained by the process according to any one of claims 10 to 12.

14. Use of the etching resist composition according to any one of claims 1 to 7, in ink-jet printing.

15. Use of the etching resist composition according to any one of claims 1 to 7, as an etching resist.

16. Use of the etching resist composition according to any one of claims 1 to 7, in the manufacture of a printed-wiring board.